UNIVERSITY OF PENNSYLVANIA

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W. A. LA LANDE, JR.

A THESIS

IN CHEMISTRY

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PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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Introduction.—Maly was probably the first to notice that rosin and abietic acid increase in weight on exposure to the air.[1] Subsequently identified as a process of autoxidation, this phenomenon has been the subject of considerable study, both in the solid acid and in solutions of the acid.[2] On the other hand, little work has been done on the obviously related subject of the autoxidation of metallic rosinates and abietates. To supply some necessary data for an investigation still in progress, the course and extent of the reaction

$$\underset{\substack{\text{solid}\\(\text{as rosinate})}}{Pb(C_{20}H_{29}O_2)_2} + O_2 \longrightarrow$$

was studied. A solution of the rosinate offers the best means of obtaining rapid and complete absorption of oxygen, but the method does not permit of the obtaining or manipulation of indisputably unchanged intermediate products. Another objection arises from the fact that the degree of absorption is somewhat affected by the solvent used. In the type of system studied in this paper, the reaction proceeds at a conveniently slow rate and the reversibility of the reaction can be directly and easily studied by submitting the reaction mixture to various changes of temperature and pressure. Lead rosinate rather than pure lead abietate was used because results obtained with it had the same significance as those obtained by using pure lead abietate. It was, therefore, unnecessary to execute the much more laborious preparation of the latter compound.

Several methods were tried for following the course of the progressive absorption of oxygen by lead rosinate. Manometric technique was found to be unsatisfactory; the results obtained were not reproducible and the final values were misleading. Frequent shaking of the sample did not improve the results. Since some of the products of the autoxidation of the rosinate liberate iodine from potassium iodide, it appeared possible to follow the course of the oxidation by an iodimetric method. This procedure required too much material and was abandoned. The gravimetric method outlined below was finally adopted as the most practical from the standpoints of convenience, accuracy and economy.

[1] Maly, *Ann.*, **161**, 115 (1872).

[2] Fahrion, *Z. angew. Chem.*, **13**, 1197 (1901); Fahrion, *ibid.*, **20**, 356 (1907); Klason and Kohler, *J. prakt. Chem.*, **63**, 337 (1906); Knecht and Hibbert, *J. Soc. Dyers Colourists*, **25**, 148 (1919); Dupont and Dubourg, *Bull. inst. pin*, **52**, 205 (1928); Dupont and Lévy, *Compt. rend.*, **189**, 763 (1929).

Experimental.—The lead rosinate used in all the experiments was prepared by the method outlined in the first part of this paper. All of the samples were taken at the same time from the same batch of material.

Samples of the rosinate of equal weight (0.4840 g.), in the form of fine powder, were weighed into glass-stoppered weighing bottles, 40 mm. in diameter and 50 mm. in height. The average thickness of the layer of rosinate was 2 mm. Each of the samples thus prepared was used immediately. The stopper of the weighing bottle was removed and the bottle was placed in the vessel shown in Fig. 2. The piece of apparatus was then transferred to the oven or thermostat, and dry preheated oxygen or nitrogen (as the experiment required) passed through at the rate of 300 cc. per hour. This rate provided a slowly but constantly changing atmosphere of the gas, without danger of loss through agitation of the powder. No attempt was made to obtain a fine temperature control, but all of the given temperatures were the same throughout a given run with a maximum variation of ±1°. Each sample was heated for a timed interval, then allowed to cool in oxygen or nitrogen, and finally weighed after six hours in the desiccator. Before each subsequent exposure to the gas the powder was mixed by rotating the stoppered weighing bottle. In the experiment carried out under pressure the weighing bottle was placed in an Emerson bomb, the pressure raised to the required amount, and the bomb then transferred to the oven.

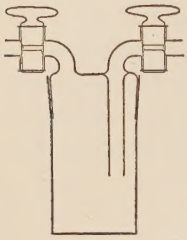

Fig. 2.

Experimental Results.—All the results recorded are average values obtained from at least two experiments conducted under precisely the same conditions.

In Table I showing the increase in weight of lead rosinate in pure dry oxygen at various temperatures, the final value in each sub-table represents the time and percentage increase in weight at which the system came to equilibrium. All runs were continued for at least one hundred hours after this point was reached in order to eliminate the possibility of a false or transient equilibrium. In each sub-table (except 125°) the data between the last result and the one immediately above it have been omitted

TABLE I

INCREASE IN WEIGHT OF LEAD ROSINATE IN OXYGEN AT VARIOUS TEMPERATURES AND AT 28° UNDER 60 ATMOSPHERES' PRESSURE

28°. Sample, 0.4836 g.			65°. Sample, 0.4835 g.		
Total hours	Total increase, g.	Increase in weight, %	Total hours	Total increase, g.	Increase in weight, %
14	0.0003	0.06	1	0.0001	0.021
32	.0013	.26	8	.0056	1.15
47	.0028	.58	26	.0104	2.15
68	.0055	1.14	40	.0128	2.65
90	.0105	2.18	71	.0146	3.02
118	.0150	3.10	95	.0155	3.20
150	.0184	3.80	114	.0162	3.35
184	.0200	4.14	156	.0173	3.57
232	.0214	4.42	204	.0182	3.76
294	.0231	4.78	252	.0186	3.84
911	.0306	6.33	398	.0196	4.05

TABLE I (*Concluded*)

100°. Sample, 0.4840 g. Total hours	Total increase, g.	Increase in weight, %	28°, 60 atm. Sample, 0.4021 g. Total hours	Total increase, g.	Increase in weight, %
3	0.0031	0.64	34	0.0066	1.63
9	.0051	1.04	93	.0149	3.71
22	.0069	1.44	141	.0201	4.77
49	.0077	1.60	189	.0235	5.63
75	.0080	1.66	240	.0253	6.33
100	.0083	1.72	307	.0266	6.62
129	.0085	1.76	362	.0282	7.01
177	.0089	1.84	410	.0297	7.38
218	.0091	1.88	460	.0298	7.42
258	.0092	1.90	508	.0307	7.63

125°. Sample = 0.4838 g.		
11	0.0002	0.041
37	.0008	.165
60	.0010	.206
84	.0016	.328
108	.0019	.391
132	.0026	.532

for space reasons. These omitted values when plotted all fall on a curve gently sloping to the maximum or final value. The calculation of the percentage increase in weight is based on the original weight of the sample. The results are plotted in Fig. 3 for the first two hundred hours.

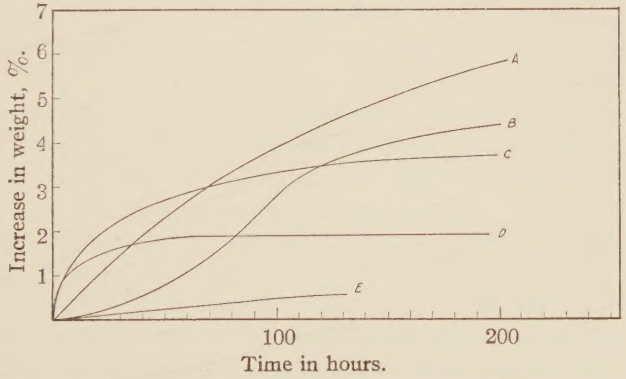

Fig. 3.—Course of the increase in weight of lead rosinate in oxygen at various temperatures and at 28° and 60 atmospheres: A, 28° at 60 atm.; B, 28°; C, 65°; D, 100°; E, 125°.

In Table II the results obtained for maximum absorption at the various temperatures are summarized. For comparison and correction, the results obtained by heating the rosinate in *nitrogen* at the various temperatures are included (Col. 2). These values represent a loss in weight, *i. e.*, the rosinate is appreciably volatile at 100 and 125°. The values for the ap-

parent oxygen absorption at 100 and 125° (Col. 3) have been corrected, in order to take into account the loss in weight of the rosinate when heated to these temperatures in an inert atmosphere. The corrected values are shown in the fourth column and represent the actual oxygen absorption. The molar equivalent of oxygen absorbed is calculated from the weight of oxygen absorbable by a rosinate containing 94.70% of normal lead abietate.

TABLE II

ABSORPTION DATA

	Change in weight, %			
T, °C.	a, in N_2	b, in O_2	a + b Oxygen absorbed, %	Molar equiv. of O_2 absorbed
28 (60 atm.)	−0.00	7.63	7.63	2.04
28	− .00	6.33	6.33	1.59
65	− .00	4.05	4.05	1.08
100	− .31	1.89	2.20	0.55
125	−1.52	0.53	2.05	.51

The relation of the apparent oxygen absorption (Table II, Col. 3) to the actual oxygen absorption (Table II, Col. 4) is shown graphically in Fig. 4.

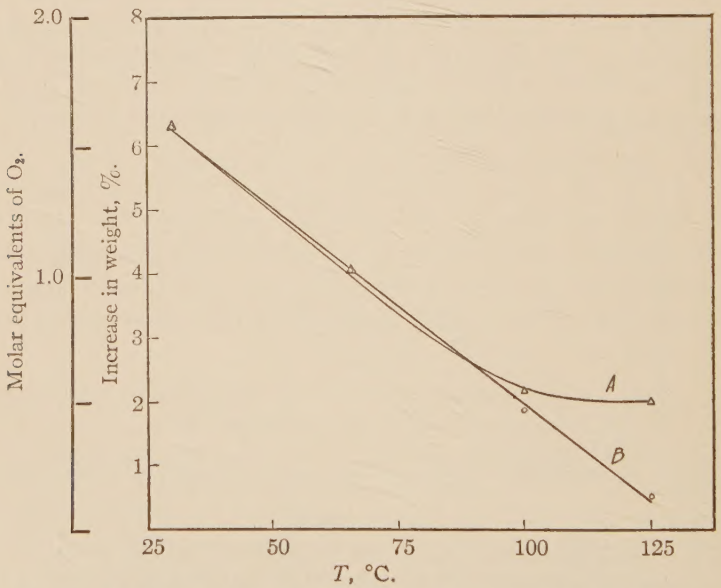

Fig. 4.—Maximum oxygen absorbed at various temperatures by lead rosinate: A, actual O_2 absorbed; B, apparent O_2 absorbed.

The results obtained after heating several of the oxidized samples in nitrogen to constant weight are reproduced in Table III. All the values determined for 100° are corrected for the slight volatility of the rosinate itself at that temperature (see Table II, Col. 2).

TABLE III

EXPERIMENTAL DATA

Oxygen originally absorbed at.....	28° (60 atm.)	28°		65°
Loss on heating in N_2 to constant weight at..	100°	65°	100°	100°
As % O_2 (of total absorbed).....	57.0	17.6	48.7	47.0
As molar equivalent of O_2.....	1.14	0.28	0.77	0.51
Molar equivalent of O_2 remaining.....	0.86	1.31	.82	.57

Discussion of Results.—The results recorded in Tables I and II show that the rate and degree of oxygen absorption by lead rosinate depend, for a given pressure, on the temperature. Dupont and Lévy[3] worked at only one temperature (60°) and it must, therefore, be assumed that this temperature was designedly or fortuitously selected since their final results indicated a sharp end-point when one mole of oxygen had been absorbed. The curve B (Fig. 3) is the familiar S-shaped curve characteristic of autocatalytic processes. The amount of oxygen absorbed at equilibrium corresponded to three atoms of oxygen. This does not necessarily indicate the formation of a compound $Pb(Ab)_2 \cdot 3O$. It is a great deal more probable that the reaction mixture at this point was a combination of all the possible reaction products, with the final product present in largest amount. The mixture slowly liberated iodine from aqueous iodide, quickly from acidified iodide. The product obtained when the experiment was repeated at the same temperature but under sixty atmospheres' pressure also liberated iodine from aqueous and acidified iodide. The results in this experiment are in good agreement with those obtained by Dupont and Lévy for abietic acid, *i. e.*, each abietate group absorbed one mole of oxygen at equilibrium.

In curves C, D and E there is again an indication that the amount of oxygen absorbed corresponded to one or two atomic equivalents of oxygen. It is more possible however, that the reaction product was a mixture. All of these oxidation products liberated iodine from aqueous iodide (very slowly) and from acidified iodide (more rapidly).

If the degree of oxygen absorption at constant pressure decreases with rising temperature, a reversibility of the initial reaction is indicated. The dissociation of the end-product (or equilibrium product) in the autoxidation of the rosinate evidently proceeds progressively as the temperature is raised. There is an indication that this dissociation is never complete, and that a maximum dissociation is reached when one atomic equivalent of oxygen remains fixed by the rosinate (Fig. 4). The amount of oxygen absorbed in each case is thus an index of the stability (and the concentration) of the end-product at a given temperature, for a constant pressure. This reasoning was applied in an experiment, the results of which are recorded in Table III. If the end-product in the autoxidation of the rosinate at a given temperature and pressure was placed in an atmosphere

[3] Dupont and Lévy, *Compt. rend.*, **189**, 763 (1929).

of lower oxygen pressure, it slowly lost weight. If, however, the temperature was raised at the lower pressure, the loss in weight occurred quickly. In the experiment, in order to increase the effect, the temperature was raised about 30° and the partial pressure of the oxygen was decreased to zero (100% nitrogen). All the oxidized samples which were treated thus still liberated iodine from iodide although the reaction was much slower compared with the action of the rosinate on the iodide before this treatment. The gas evolved from the oxidized samples was passed over anhydrous copper sulfate and bubbled through barium hydroxide and palladous chloride solutions. There was no indication of the color or turbidity which water, carbon dioxide and carbon monoxide would have produced with these reagents. The gas evolved from two half-gram samples of the oxidized rosinate was passed through the heated, packed tube of a combustion furnace. The effluent gas was received in barium hydroxide solution. No turbidity was observed. The author thus feels justified in assuming that the gas evolved from the oxidized rosinate was pure oxygen. The rosinates again absorbed oxygen when exposed to the gas, but very slowly, an effect undoubtedly due to the change in surface produced by a slight sintering of the powder at the higher temperatures. It was believed before the experiment was tried that the relative amount of oxygen lost and the actual amount remaining fixed would be the same in each case. This would have proved decisively that a stable oxygen compound was formed during the autoxidation. The data obtained (Table III) were not in sufficiently good agreement to be interpreted as substantiating this belief. It is possible that such a compound was formed, but in an amount depending on the conditions of the particular experiment. Hence the amount of oxygen remaining fixed would vary. Another explanation of the apparent non-existence of a relationship among the values obtained for the amount of oxygen remaining fixed at zero oxygen pressure is the possibility of an immeasurably slow but positive dissociation of the more stable oxygen compounds formed during the autoxidation. In other words, these values would approach each other if the conditions were maintained for a sufficiently long time.

According to Dupont and Lévy the autoxidation of abietic acid is accomplished through the agency of an intermediate oxide $HAbO$, and a peroxide $HAbO{\cdot}O_2$, the final product being $HAbO_2$. Unfortunately, the action of this final product on an iodide solution was not investigated. If the autoxidation of lead rosinate proceeds by a similar mechanism, two moles of oxygen should be absorbed by one mole of lead abietate. Actually, this result was obtained in only one instance (Table II), *i. e.*, under the most extreme conditions tried, and the product readily oxidized iodide. This would indicate that the end-product itself is capable of acting as an oxidizer, or that the product obtained under the most extreme conditions

(28°, 60 atm.) was still an equilibrium mixture of end-product and intermediate peroxides. The most obvious interpretation of the data obtained in this investigation would favor the latter conclusion.

The writer takes this opportunity to thank Professor H. S. Lukens for help and suggestions obtained from him during the course of this work. Thanks are also due Mr. J. G. Butz for helpful suggestions.

Summary

The course, extent and reversibility of the autoxidation of lead rosinate has been studied, using a carefully prepared rosinate of known composition.

The results have been discussed from the viewpoint of the theory suggested by Dupont and Lévy for the autoxidation of abietic acid.